Effect of commercial and synthesized multiwalled carbon nanotubes on the electrical and thermal properties of polystyrene

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ABSTRACT

Multiwalled carbon nanotubes (JMWCNTs) were synthesized using varying amounts of ferrocene catalyst (5-8 wt% of hydrocarbon precursor) and *Jatropha* seed oil as hydrocarbon precursor by chemical vapour deposition (CVD). The synthesized carbon material revealed highly entangled MWCNTs with some amount of amorphous carbon with very few defects. The range of product yield (compared to total weight of hydrocarbon source) was 20 - 28 % being highest in the case of nanotubes produced using 7 % (w/w) catalyst. The carbon nanotubes prepared by this method had diameter ranging from 50-100 nm and lengths from hundreds of nanometres to several micrometers. A decrease in diameter of nanotubes was observed along with increase in catalyst content upto 7% (w/w). The morphology of nanotubes synthesized was studied by high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM) and Raman spectroscopy. The effect of above prepared nanotubes and commercial multiwalled carbon nanotubes (CMWCNTs) on electrical, thermal, barrier and morphological properties of polystyrene was studied. Polystyrene nanocomposites prepared with JMWCNTs gave better improvement in properties as compared to nanocomposites prepared using CMWCNTs.

INTRODUCTION

CNTs have gained lot of applications in the field of chemistry, physics, nanotechnology and as filler in polymer matrix system due to their promising properties. In general, CNTs can be produced from hydrocarbons by arc discharge (AD), chemical vapour deposition (CVD), pulsed laser vaporization (PLV) and high-pressure carbon monoxide conversion method (HPCo). AD and PLV methods produce high quality carbon nanotubes with minimal impurities but the high temperature employed for the evaporation of carbon atoms from solid sources and lesser yield makes it difficult to scale up these processes in a cost effective manner.

Various researchers have used different hydrocarbon sources for the production of carbon nanotubes such as toluene [1], xylene [2], and ethylene [3] by CVD. Although products from petroleum refinery are being widely used as hydrocarbon precursor for the production of nanotubes but there seems to be a limitation to these products. Therefore, it was considered of interest to explore the use of a novel, cheap and green energy source *Jatropha* oil for the production of multiwalled carbon nanotubes. *Jatropha* oil is obtained from the seeds of *Jatropha curcus*, a plant grown in the tropical climate.

The first part of the present paper focuses on the optimization of conditions such as catalyst content on the yield (%) and quality of CNTs.

Various researchers have prepared PS/nanotube nanocomposites using different methods such as solution blending [4–7], in-situ polymerization [8,9] and melt blending [10].The second part of the research paper presents the use of CNTs for the production of polystyrene-CNTs nanocomposites by solution blending and evaluating its effect on the electrical and thermal properties of polystyrene. The results were compared with nanocomposites prepared using commercial nanotubes.

EXPERIMENTAL

The crude *Jatropha* oil was procured from "Jatropha Vikas Sansthan", New Delhi, India. Ferrocene was purchased from ACROS Organics, New Jersey, USA. Commercial carbon nanotubes (outer diameter = 20-30nm, length 10-20µm) were purchased from cheap tubes, USA. A commercial product polystyrene SC206 was purchased from Supreme Petrochem limited (manufacturer of polystyrene under technical collaboration of Chemical Corp. and ABB Lummus Crest of USA). The melt flow index and softening point were 11.5 [200^{o}C and 2.16kg load] and 101^{o}C respectively.

Multiwalled carbon nanotubes were grown by thermal decomposition of Jatropha oil in the presence of iron catalyst using two zone furnace with temperature of 450°C in first zone and 800°C in the second zone. Once the temperature was reached, the solution containing a mixture of ferrocene and *Jatropha* oil (in different proportions) was injected in the reactor at a point where the temperature was 450°C. CNTs prepared using varying amount of catalyst i.e. 5, 6, 7 and 8% were designated as CNT5c, CNT6c, CNT7c and CNT8c respectively.

Polystyrene nanocomposites were prepared by solution blending method using toluene as solvent. For this purpose, required amounts of carbon nanotubes (CNT7c) was dispersed in toluene with the help of mechanical stirring followed by sonication. The nanotubes dispersed in toluene were mechanically stirred for 24 h followed by sonication for 4h (50 W, 20 kHz). The above suspension was mixed with polystyrene dissolved in toluene and then mechanically stirred for 48h followed by ultrasonication for 4h (50 W, 20 kHz). An appropriate amount of the suspension was poured onto a glass plate to prepare a film of thickness ~1mm. The suspension was allowed to dry at room temperature for 24 h, followed by drying in vacuum oven at 80 °C to remove any residual toluene. In order to classify the type of nanotubes used for nanocomposite preparation PSJC and PSCC have been used as designation indicating nanocomposites prepared using multiwalled carbon nanotubes from Jatropha seed oil and commercial multiwalled carbon nanotubes respectively. Further to indicate the amount of nanotubes, numerals 01, 10, 20, 30, 40, and 50 have been suffixed to the designation for samples having 0.1, 1.0, 2.0, 3.0, 4.0 and 5.0 phr of CNTs respectively.

Morphological characterization of CNTs was done using EVO50 (80kV) scanning electron microscope (SEM), Zeiss (100kV) transmission electron microscope (TEM) and Technai G20-stwin (200 kV) high resolution transmission electron microscope (HRTEM).

Qualitative analysis of purified nanotubes was done using (ZEISS EVO 50) EDX analysis with an operating voltage of 20kV and Raman spectroscopy at Ar laser of wavelength 514.5 nm. TA instrument Q-50 TGA was used for recording TG traces in air atmosphere for as produced carbon nanotubes at a flow rate of 60cm^3/min. The TGA studies were also used to analyse whether other forms of carbon were present in the soot deposits or not.

Polystyrene nanocomposites were characterized for their electrical, thermal and morphological properties. The electrical conductivity of the nanocomposites (length = 10mm, width 15mm, thickness = 1mm) at room temperature was measured by four point contact method using a Keithley 224 programmable current source for providing current, the voltage drop was measured by Keithley 197A auto ranging digital microvoltmeter. Electrical conductivity is measured as the inverse of resistivity.

$$\text{Electrical conductivity } (\Omega^{-1}\text{cm}^{-1}) = \frac{\text{Probe distance (cm)} \times \text{current in milliampere}}{\text{width (cm)} \times \text{thickness (cm)} \times \text{voltage drop}}$$

The values were averaged over five readings of voltage drops at different portions of the sample.

Q-50 TGA was used for recording TG traces in nitrogen atmosphere for PS/nanotube nanocomposites, at a flow rate of 60cm^3/min. Perkin Elmer Pyris 6 Differential Scanning Calorimeter was used for recording DSC scans of PS/nanotube nanocomposites. Morphology of nanocomposites was studied using Zeiss (100kV) transmission electron microscope (TEM)

RESULTS AND DISCUSSION

Characterization of carbon nanotubes. For all the samples prepared, the carbon filaments observed were highly entangled and abundant. SEM micrographs (Fig.1) showed the formation of filaments/fibres enhanced with increasing amounts of catalyst. Also an increase in length of filaments was observed with increasing amount of catalyst up to 7 % (w/w). Further increase of catalyst showed a deteriorating effect on the quality of CNTs.TEM micrographs (Fig.2) showed that with increase in catalyst content up to 7% (w/w) diameter of nanotubes was decreased. However, higher aspect ratio was found for CNT6c due to their larger length as compared to CNT7c.Further HRTEM images (Fig. 3) confirmed the formation of multiwalled carbon nanotubes.

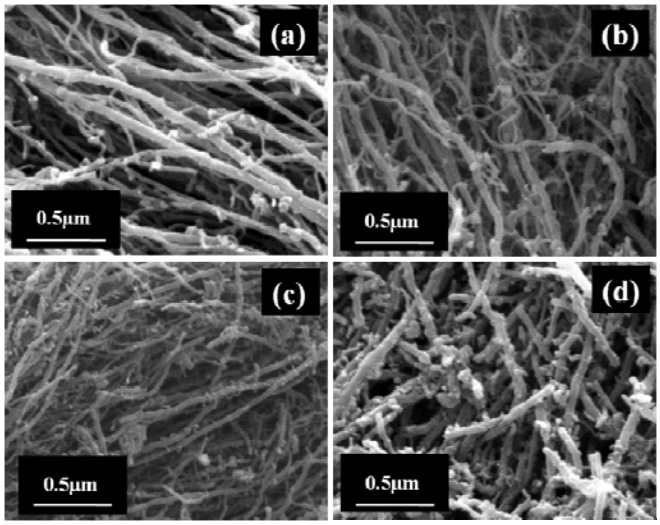

Fig 1.: SEM images of the as-synthesized carbon filaments bycatalytic decomposition of Jatropha seed oil (a) CNT5c (b) CNT6c (c) CNT7c (d) CNT8c

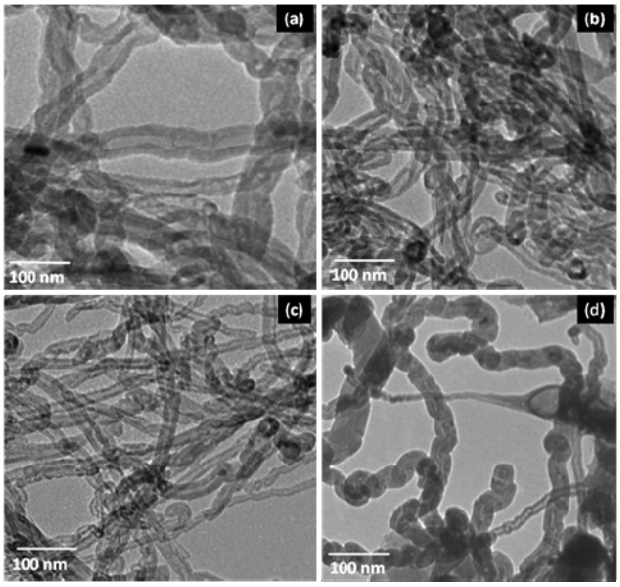

Fig 2: TEM images for (a) CNT5c, (b) CNT6c, (c) CNT7c and (d) CNT8c

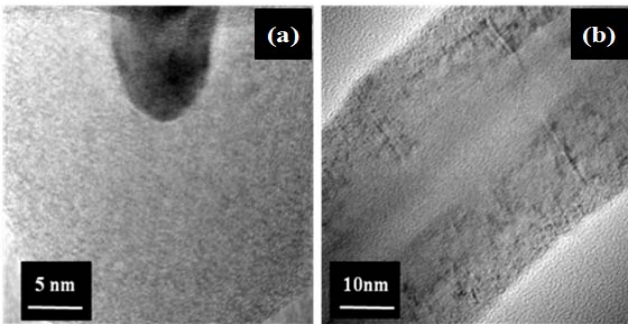

Fig 3. HRTEM images for (a) CNT6c and (b) CNT7c

TGA analysis of as-synthesized nanotubes showed that CNT5c had approximately 20-30% of amorphous carbon as mass loss observed in the temperature range 350-375°C. Shi et al [11] and Hartyunyan et al [12] have also reported the initial oxidation of amorphous carbon to begin at 364°C and 350°C respectively. There is no mass loss beyond 395°C up to 540°C. Further a sharp peak was observed from 540°C to 650°C indicating degradation of graphitic nanoshells. The gasification is finished at this stage with maximum degradation temperature being 575°C and a residue is obtained corresponding to metal impurity present in the sample. For sample CNT6c and CNT7c, there is a very little mass loss in the temperature range of 350°C-400°C indicating the presence of very less amorphous carbon material. CNT6c and CNT7c started gasification at 575°C and 595°C respectively and ended at 650°C and 700°C respectively. The maximum degradation temperature is 605°C and 630°C for CNT6c and CNT7c respectively. In case of CNT8c (with the highest amount of catalyst), it was observed that soot material first starts to gain wt in the range 300°C -350°C followed by degradation at 375°C corresponding to ~30% mass loss. The weight gain can be attributed to oxidation of Fe catalyst particles present in the soot material. Hou et al [13] also reported weight gain of soot material at temperatures below 340°C and explained it in relation to oxidation of catalyst particles. Further degradation at 375°C corresponding to 30% mass loss indicates that there is la arge amount of amorphous carbonaceous material present in this sample. Further it was observed in all the samples except CNT8C, that there was not weight gain below 350°C. However, the absence of weight gain in the samples CNT5c, CNT6c and CNT7c is due to the fact that the catalyst particles are encapsulated in the nanotubes formed. This has been supported by HRTEM analysis as well which shows the nanotube tip with encapsulated catalyst particles (Fig.3).The yield of carbon nanotubes was calculated for purified nanotubes (by oxidation at 350°C for 4h) and was found to be maximum for CNT7c. Further EDX analysis of purified nanotubes supported SEM and TGA data confirming maximum % of carbon in case of CNT7c. Results of EDX-analysis are shown in Table 1.

Table 1. EDX-spectrum Analysis for JMWCNTs

Sample Designation	Carbon content (%)	Iron content (%)	Oxygen content (%)
CNT5c	84.00	4.94	11.96
CNT6c	86.00	5.98	8.02
CNT7c	87.00	6.87	6.13
CNT8c	81.62	7.00	11.38

Fig.4 shows the Raman spectrum measured with Ar laser of wavelength 514.5 nm on the as-synthesized MWCNTs material. The peaks at 1601cm^{-1}, 1582 cm^{-1}, 1571 cm^{-1} and 1562 cm^{-1} for CNT5c, CNT6c, CNT7c and CNT8c respectively, correspond to an E_{2g} mode of graphite and is related to the vibration of SP^2-bonded carbon atoms in a two dimension hexagonal lattice, such as in a graphite layer [14]. The peaks at 1374 cm^{-1}, 1361 cm^{-1}, 1351 cm^{-1} and 1349cm^{-1} for CNT5c, CNT6c, CNT7c and CNT8c respectively, are associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite [15]. The position of the D line (disorder induces

mode) in the region of 1300-1400 cm^{-1} confirms the presence of MWCNTs as shown by Jinquan and co-workers [16]. Further peaks in low frequency region i.e. 100-600 cm^{-1} region (Radial Breathing Mode) correspond to atomic vibrations of carbon atoms in the radial direction. It has been stated in the literature that vibration frequency of the Radial Breathing Mode is inversely proportional to the diameter of single walled nanotubes. The following expression w = 224/d + 14 is used to calculate the diameter of single walled nanotubes, where w is Radial Breathing Mode frequency and d is the diameter of the nanotube in nanometre [9] For multiwalled nanotubes this value corresponds to the diameter of the innermost tube [17]. The diameter of innermost tube for all the MWCNTs synthesized was calculated using the above equation. The nanotubes synthesized with 7% catalyst content had the least inner diameter being 1.85nm followed by 1.93 nm for 6% catalyst content and 1.95 nm for 5% catalyst content. However, with 8% (w/w) catalyst content, the inner diameter of carbon nanotubes increased, this was also supported by TEM images (Fig.2).

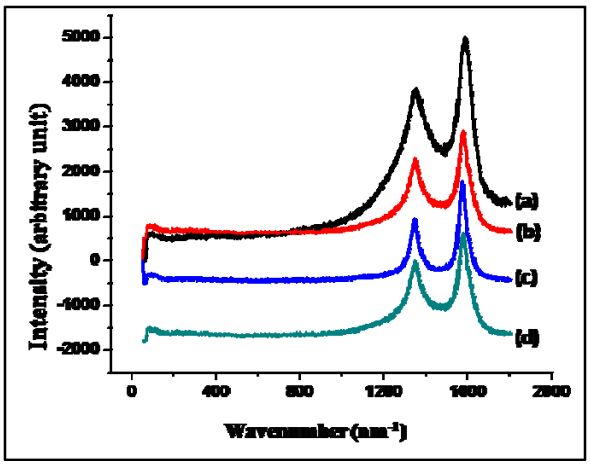

Fig.4. Raman Spectrum of the as prepared JMWCNTs (a) CNT5c, (b) CNT6c, (c) CNT7c and (d) CNT8c

Characterization of PS/nanotube nanocomposites. Fig.5 shows the effect of commercial multiwalled carbon nanotube content on the electrical conductivity of nanocomposites. As shown in Fig.5, with 0.1phr loading of CMWCNTs, PS nanocomposites showed electrical conductivity of 0.0012 S/cm. Electrical conductivity increased to 0.017 S/cm, 0.023 S/cm, 0.033 S/cm , and 0.034 S/cm for nanocomposites having CNT content 1.0, 2.0, 3.0 and 4.0 phr respectively. With further increase in nanotube content up to 5.0 phr, electrical conductivity did not show much increase. Fig. 6 further shows the effect of synthesized nanotube [JWCNT (CNT7c)] content on the electrical conductivity of PS/nanotube nanocomposites.

With the addition of 0.1phr JMWCNTs, PS nanocomposites showed conductivity of 0.09S/cm. With further increase in nanotube content conductivity for PS nanocomposites was raised to 0.15 S/cm which is 10 fold more as compared to sample prepared with 0.1 phr loading. PS/JMWCNTs nanocomposites also showed increase in conductivity with increase in CNT loading up to 3phr. PS/nanotubes nanocomposites showed 0.19 S/cm, 0.25 S/cm, 0.26 S/cm and 0.27 S/cm conductivity with the addition of 2, ,3, 4 and 5phr nanotube content respectively. Electrical conductivity did not show much increase after 3phr nanotube content. PS/nanotube nanocomposites prepared with JMWCNTs (CNT7c) showed better electrical conductivity values as compared to nanocomposites prepared with commercial nanotubes Commercial nanotubes have diameter 20-30nm with length 10-20µm only, whereas, nanotubes synthesized using *Jatropha* seed oil with 7% (w/w) catalyst had diameter ranging from 20-35nm with length of around 100 µm. Therefore, synthesized nanotubes had higher aspect ratio as compared to commercial nanotubes. The higher aspect ratio of nanotubes provides a better network inside polystyrene matrix or a channel at a lower concentration of CNT %. Singh and co-workers [18] also showed better electrical conductivity for nanocomposites prepared with nanotubes having higher aspect ratio.

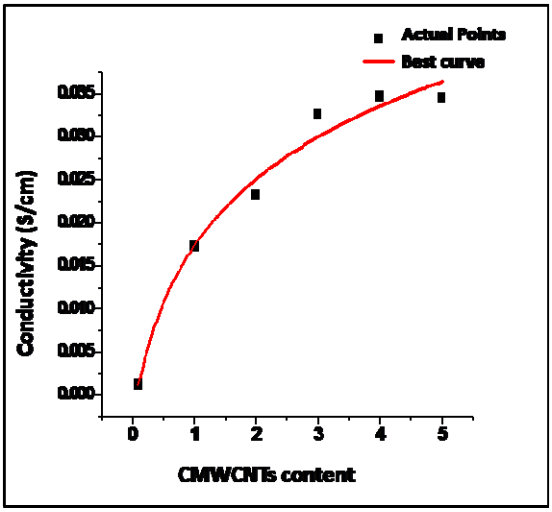

Fig 5. Effect of CMWCNTs Content on Electrical Conductivity of PS/CMWNTs Nanocomposites

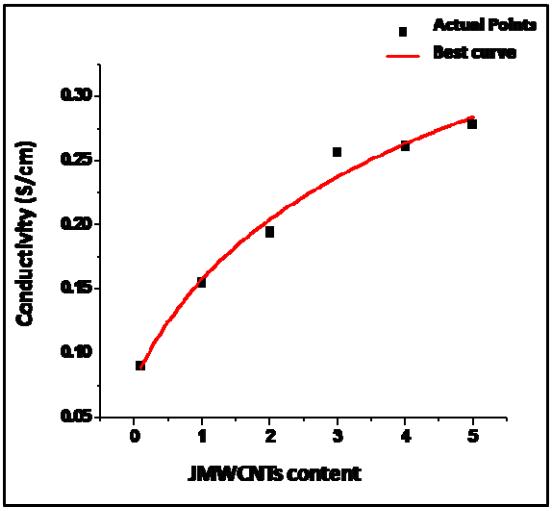

Fig. 6: Effect of JMWCNTs Content on Electrical Conductivity of PS/JMWNTs Nanocomposites

The relative thermal stability of nanocomposites prepared using JMWCNT or CMWCNT was compared by comparing T_{10} (temperature at which 10% mass loss was observed), T_{50} (Temperature for 50% mass loss) and T_{max} (temperature at which rate of mass loss is maximum). The effect of commercial and synthesized nanotubes content on $T_{10,}$ T_{50} and T_{max} temperatures as depicted from TG/DTG curves is shown in Table 2. All these temperatures showed an increase upon incorporation of carbon nanotubes. By the addition of 0.1 phr nanotube only, T_{10} was increased from 362ºC for neat polystyrene to 368 ºC for PSCC-01 and 369 ºC for PSJC-01. With same nanotube content, T_{50} was increased from 403 ºC for neat PS to 410 ºC and 412 ºC for PSCC-01 and PSJC-01 respectively. Further T_{max} was increased from 383 ºC for neat PS to 392 ºC and 394 ºC PSCC-01 and PSJC-01respectively. Similar observation was made when higher nanotube content was used. PS nanocomposites prepared with synthesized nanotubes showed better improvement in thermal property of polystyrene. The nanotubes synthesized in our

laboratory showed better thermal stability due to presence of many layers of walls in the nanotube structure (as shown in HRTEM) images.

The glass transition temperatures of polystyrene and polystyrene nanocomposites prepared using commercial nanotubes and synthesized nanotubes was determined by recording DSC scans. In all the DSC scans, an endothermic shift in the baseline was observed. The glass transition temperature was noted as midpoint inflexion and the results are summarized in Table 3.

Table 2. Effect of Nanotube Content on Thermal Properties of Polystyrene

Sample Designation	T_{10}(°C)	T_{50} (°C)	T_{max} (°C)
PS neat	403	383	362
PSJC-01	369	412	394
PSJC-10	371	416	400
PSJC-20	376	417	404
PSJC-30	379	418	408
PSJC-40	382	419	411
PSJC-50	384	421	425
PSCC-01	368	410	392
PSCC-10	371	412	398
PSCC-20	374	414	403
PSCC-30	376	416	406
PSCC-40	379	418	407
PSCC-50	382	420	418

Tg of polystyrene increased with increasing amount of nanotube. There was a significant increase in Tg of polystyrene by the addition of 5 phr synthesized nanotubes.

Table 3: Glass Transition Temperature for PS/nanotube Nanocomposites Prepared with Commercial and Synthesized Nanotubes [Tg of neat PS = 91 °C]

Sample Designation	T_g(°C)	Sample Designation	T_g(°C)
PSJC-01	95	PSCC-01	91
PSJC-10	101	PSCC-10	92
PSJC-20	102	PSCC-20	99
PSJC-30	102	PSCC-30	100
PSJC-40	104	PSCC-40	101
PSJC-50	108	PSCC-50	104

Morphology of PS nanocomposites was studied by TEM analysis. TEM analysis of PS nanocomposite film (70nm thick) with 5 phr nanotube content was carried out for both types of nanotubes. Fig.7 shows the TEM images for sample PSCC-50 and PSJC-50. TEM images clearly show that commercial nanotubes are smaller in length as compared to synthesized nanotubes. Due to this continuous network was not formed in case of nanocomposites prepared with commercial nanotubes. However, synthesized nanotubes are elongated and connected to each other inside the polymer matrix. This explains better improvement in electrical conductivity of nanocomposites prepared with synthesized nanotubes.

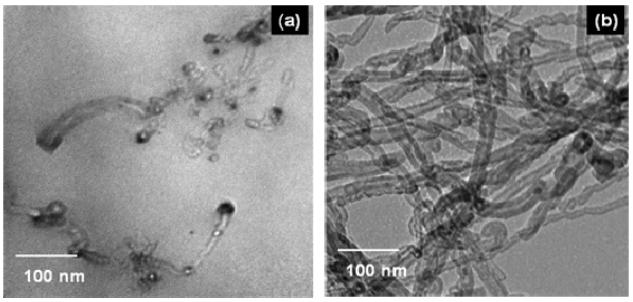

Fig 7. TEM images for PSCC-05 and PSJC-05

CONCLUSION

Multiwalled carbon nanotubes were successfully synthesized by CVD using Jatropha seed oil as hydrocarbon precursor. The optimized amount of catalyst was found to be 7% (w/w).

The increase in conductive and thermal properties of polystyrene was better with the incorporation of nanotubes synthesized using *Jatropha* seed oil than using commercial available nanotubes.

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